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$ThMn_{12}$-type structure and uniaxial magnetic anisotropy in $ZrFe_{10}Si_2$ and $Zr_{1-x}Ce_xFe_{10}Si_2$ alloys

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ABSTRACT

Arc-melted $(Zr_{1-x}Ce_x)_{1.1}Fe_{10}Si_2$ alloys were found to crystallize into a pure or nearly pure $ThMn_{12}$ structure for $0 \leq x \leq 0.6$. At room temperature, the alloys exhibit ferromagnetism with an uniaxial magnetocrystalline anisotropy. Metastable $ZrFe_{10}Si_2$ compound possesses room-temperature saturation magnetization of at least 11 kG and Curie temperature of 325 °C; both properties slightly decrease when Ce is being substituted for Zr. The anisotropy field, on the other hand, increases with the Ce from 16.9 to 24 kOe at $x = 0.6$. These intrinsic magnetic characteristics as well as the absence of expensive rare-earths and Co make the compounds interesting for development of low-cost permanent magnets. At $0.7 \leq x \leq 0.8$, the $ThMn_{12}$ structure was found to co-exist with the Th_2Ni_{17}-type structure, whereas the equilibrium Th_2Zn_{17}-type structure was observed only at $x = 1$. Prepared under similar conditions $Hf_{1.1}Fe_{10}Si_2$ alloy does not crystallize into the $ThMn_{12}$-type structure.

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1. Introduction

Tetragonal $R(Fe,M)_{12}$ compounds with R standing for rare earth elements have long been of interest as permanent magnet materials [1]. In recent years, concerns about supply of the raw rare earths motivated intensifying search for the rare-earth-lean and rare-earth-free hard magnetic materials which would not necessarily surpass the $Nd_2Fe_{14}B$, but nevertheless could "bridge" the performance gap presently existing between the ferrite and Nd–Fe–B magnets [2]. The $R(Fe,M)_{12}$ compounds are already "rare-earth-lean" compared to the R–Fe–B and R–Co permanent magnet materials. To fully explore this advantage, a particular attention has been recently paid to synthesis of these compounds with the most abundant and least "critical" rare earth, cerium [3–5]. Although the mixed-valent state of the Ce atoms is known to have an unfavorable effect on the Curie temperature T_C of the Ce–Fe compounds, Zhou et al. [4] reported an unexpectedly high T_C of the 1:12 structure (the $ThMn_{12}$ type) in $CeFe_{10}Si_2$ – together with a uniaxial, if not very strong, magnetocrystalline anisotropy. This important observation was made for the multiphase alloy prepared via melt spinning, a non-equilibrium technique. *Ab initio* calculations by Drebov et al. [6] had led to a tentative conclusion that the tetragonal $CeFe_{10}Si_2$ structure is stable. At the same time, the available experimental data [7–12] confirm stability of the tetragonal $R(Fe,Si)_{12}$ structures only for the rare-earth and actinide R having an atomic radius equal or smaller than 0.181 nm (Sc, Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu and U). Sakurada et al. [13] proposed a model according to which stability of the 1:12 structure in the $R(Fe,Si)_{12}$ alloys depends on the *average* radius of the atoms in the R sites (the 2a sites); they demonstrated stabilization of this structure when part of the larger Nd atoms in the $RFe_{10}Si_2$ was replaced with the smaller Zr atoms. The 1:12-structure-stabilizing effect of Zr is evident even in the case of the Sm atoms (the "borderline" atomic radius of 0.181 nm): unlike the $SmFe_{10}Si_2$, cast $Sm_{0.7}Zr_{0.3}Fe_{10}Si_2$ alloys were found to crystalize directly into the 1:12 structure [14]. In fact, Zr and Hf are the only non-rare-earth and non-actinide R known to form the tetragonal $R(Fe,M)_{12}$ compounds. However, the two such compounds reported to date, $ZrFe_{12-\delta}Al_\delta$ and $HfFe_{12-\delta}Al_\delta$, exist at large δ values (6–7) and they do not exhibit a room-temperature ferromagnetism [15]. As for the Zr–Fe–Si system, the available phase diagrams [16,17] feature no equilibrium 1:12 structure at 800 °C, 1000 °C and 1100 °C.

The work presented in this report began as an attempt to study Zr substitution for Ce in the $CeFe_{10}Si_2$ alloys. To the authors' surprise, the 1:12 structure was easily obtained not only in the quaternary alloys, but also in the ternary $ZrFe_{10}Si_2$. Thus, the magnetic properties of the new $Zr_{1-x}Ce_xFe_{10}Si_2$ series of the 1:12 compounds

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are reported together with discussion of their stability and application prospects.

2. Experiment

Alloys with the nominal compositions $(Zr_{1-x}Ce_x)_{8.4}Fe_{76.2}Si_{15.4}$ with $x = 0$, 0.2, 0.4, 0.6, 0.7, 0.8, 1.0 and also a $Hf_{8.4}Fe_{76.2}Si_{15.4}$ alloy were prepared as 2.5 g ingots by arc-melting the pure components on a water-cooled copper hearth. Selected alloys were additionally annealed at 1000 °C (in argon-filled quartz capsules; quenched in water). Ingot surfaces, likely to contain impurities, were machined off prior to characterization. Densities of the alloys were determined with the water-immersion techniques (the Archimedes method). Powders for X-ray diffraction (XRD) and room-temperature magnetic measurements were prepared with a hand mortar. Oriented powders were immobilized with epoxy resin (for the XRD) or with paraffin wax (for the magnetic measurements) under a magnetic field of 16–19 kOe. XRD determination of the crystal phases was performed with a Rigaku Ultima IV diffractometer at the CuKα radiation. The XRD results were analyzed with Powder Cell software [18]. Scanning electron microscopy (SEM; a JEOL JSM-6335F instrument) and energy-dispersive spectrometry (EDS; an IXRF Systems instrument) of polished unetched alloy samples were employed to clarify the nature of minority phases. The magnetic measurements were done with a Quantum Design VersaLab vibrating sample magnetometer. Thermomagnetic data were obtained at a field of 5 kOe for small (≈10 mg) ingot pieces. Room-temperature magnetization-vs-field data for the oriented powders were corrected for self-demagnetization using demagnetization factors determined for similarly prepared Fe powders.

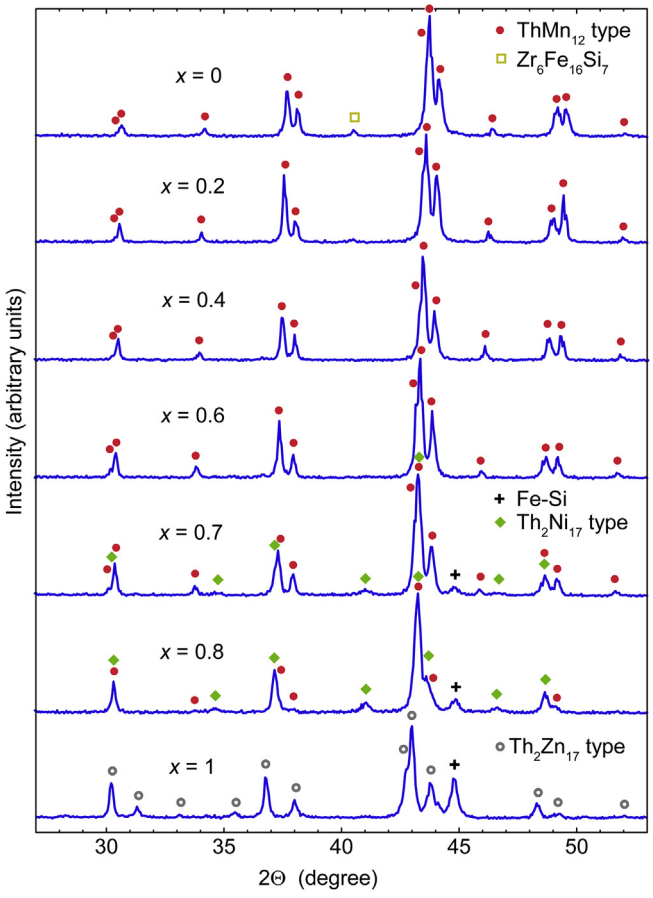

Fig. 1. Powder XRD spectra of $(Zr_{1-x}Ce_x)_{1.1}Fe_{10}Si_2$ arc-melted alloys.

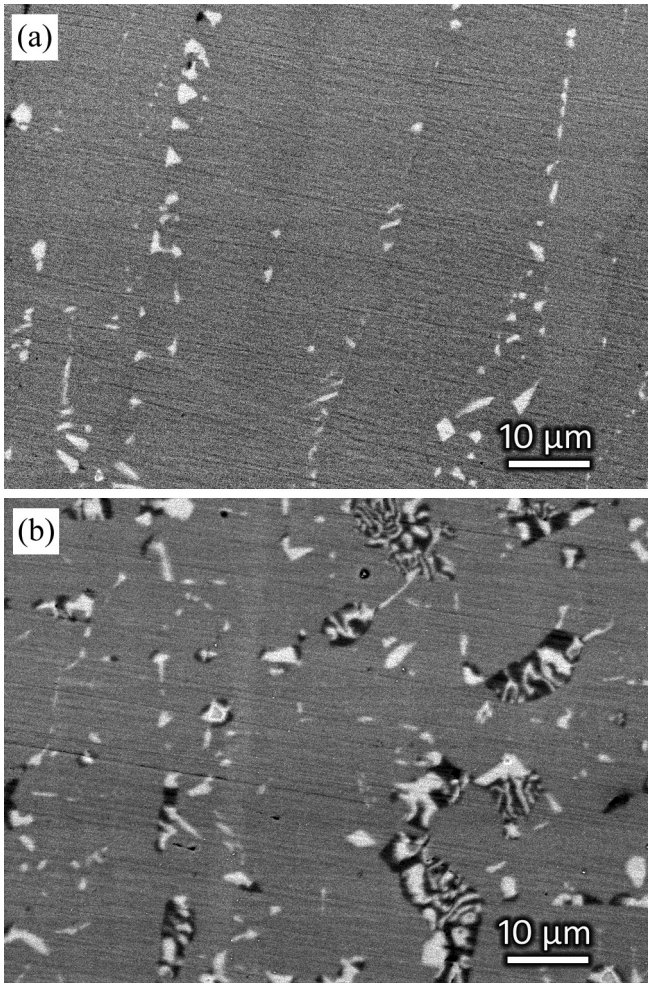

Fig. 2. Backscattered electrons SEM micrographs of $Zr_{1.1}Fe_{10}Si_2$ arc-melted alloy: (a) as-made, (b) additionally annealed for 20 h at 1000 °C. Lighter inclusions: $Zr_{19}Fe_{57}Si_{24}$; darker inclusions: $Fe_{88}Si_{12}$.

3. Results

XRD spectra of the as-made alloys are presented in Fig. 1. The ternary $ZrFe_{10}Si_2$ sample features the 1:12 structure coexisting with 3–5 vol.% of the cubic $Zr_6Fe_{16}Si_7$ structure (the $Mg_6Cu_{16}Si_7$ type, space group $Fm\bar{3}m$, $a = 1.157$ nm). The latter phase appears as lighter inclusions in the backscattered electrons SEM image shown in Fig. 2(a). The 1:12 becomes the only detectable structure in the Ce-substituted $(Zr_{1-x}Ce_x)_{1.1}Fe_{10}Si_2$ alloys when $0.2 \leq x \leq 0.6$. Further Ce substitution results in emergence of $(Ce,Zr)_2(Fe,Si)_{17}$ and

Table 1
Approximate volume percentage of crystalline phases observed in arc-melted $(Zr_{1-x}Ce_x)_{1.1}Fe_{10}Si_2$ alloys with $x \geq 0.6$.

x	Structure			
	1:12	2:17H	2:17R	bcc
0.6	100	0	0	0
0.7	57	36	0	7
0.8	24	69	0	7
1.0	0	0	79	21

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